

DESCRIPTIVE ABSTRACT

SOLID AQUEOUS GEL COMPRISING A HYDROPHILIC GELLING AGENT, A CELLULOSE DERIVATIVE AND PIGMENTS AND/OR PEARLESCENT AGENTS AND ITS USES

The present invention relates to a solid aqueous gel, characterized in that it comprises i) at least one hydrophilic gelling agent, ii) at least one cellulose derivative and iii) a pulverulent phase comprising at least one pigment and/or one pearlescent agent, the combination of the hydrophilic gelling agent and of the cellulose derivative being present in the gel in an amount of less than or equal to 20% by weight relative to the total weight of the gel.

This gel may be used in stick or compact (waterpact) form and can constitute make-up products for the skin and/or the mucous membranes and/or the keratinous fibres. This gel has the advantage of being stable (absence of syneresis). It allows easy and homogeneous disintegration of the product and provides great freshness upon application.

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**SOLID AQUEOUS GEL COMPRISING A HYDROPHILIC GELLING
AGENT, A CELLULOSE DERIVATIVE AND PIGMENTS AND/OR
PEARLESCENT AGENTS AND ITS USES**

5 The present invention relates to a solid aqueous gel, as well as its use in the cosmetics field, in particular as a make-up and/or health care product for the skin and/or the mucous membranes and/or the keratinous fibres.

10 Products which exist in solid form are known in the cosmetics industry. As products of this type, there may be mentioned, for example, in the make-up field, eyeshadow, foundation or lip sticks; in the field of skin or lip care, pencils for repairing the
15 lips, depigmenting, make-up-removing or moisturizing sticks; in the field of hygiene, deodorant sticks, foam sticks or cakes for shaving or for washing the skin.

 It is indeed particularly advantageous to have products in the form of sticks since such products
20 are very convenient to use, they are easy to carry and there is no risk of the product running.

 Moreover, make-up products are fairly generally formulated on the basis, on the one hand, of a fatty phase because of considerations of comfort and
25 smoothness and, on the other hand, of a pulverulent phase which provides the desired colour. This pulverulent phase may comprise pigments and/or fillers

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and/or pearlescent agents. The fatty phase generally comprises waxes and/or oils and/or pasty compounds.

However, formulated sticks based on waxes have certain disadvantages: they have a greasy character which is not appreciated by users and they lack freshness on application. In addition, it is difficult to introduce hydrophilic active agents therein.

Efforts are therefore being increasingly made to produce make-up sticks comprising an aqueous phase in the highest concentration possible. It is of course known to produce nongreasy sticks such as deodorant sticks, but the latter are often formulated with soaps such as stearates of sodium hydroxide or of triethanolamine as gelling agent and they thus have a basic pH which is aggressive for the skin and is poorly compatible with the make-up pigments.

Moreover, the presence of pigments or of pearlescent agents in aqueous sticks causes problems of disintegration of the product, that is to say of collecting of the product: indeed, these pigments and/or these pearlescent agents, which are essential for make-up products to provide colour, are solid particles which are not solubilized in the final composition. Because of this, they may interfere with the stability of the latter.

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However, it is essential, for a make-up product in particular, that the product is collected in an ideal manner, that is to say allows, in a simple manner, by means of the finger or a sponge or even
5 directly on the skin of the body for example, not only the appropriate quantity of product (not too much so as not to unnecessarily waste the product but enough to allow a make-up effect) to be collected but also the integrity of the product to be preserved at the time it
10 is collected: the product should not be broken through a phenomenon of shearing but the whole product should be collected with the pigments and/or the pearlescent agents, and/or optionally the fillers, which provide the make-up function. It is only on this condition that
15 the application of the product can be made homogeneously and the make-up obtained will be uniform.

Stable solid aqueous gels comprising pigments are known; but these products are generally impossible to disintegrate; they are often brittle; it is
20 therefore impossible to collect the product on the finger or on a sponge. Such products do not allow a homogeneous film to be deposited on the skin.

Products which can be disintegrated also exist but they are, in this case, too soft and sheared
25 during repeated applications or exhibit phenomena of syneresis over time, that is to say that the liquid portion exuded and the product has two phases: a solid

phase which cannot disintegrate and a liquid phase. The product can no longer perform its function, namely acting as make-up, since it is impossible to collect the pigments on the finger or on a sponge.

5 Aqueous rigid gels are described in the documents WO-A-97/17055 and WO-A-97/17053. However, these gels require the use of a fairly high concentration of gelling agent and involve a special preparation technique, extrusion. In addition, the
10 sticks described in the document WO-A-97/17055, because of the high concentration of gelling agent, lack freshness and smoothness during application to the skin, and those described in the document WO-A-97/17053 have to be hydrated at the time of use. Furthermore,
15 these gels often become brittle over time and no longer exhibit a good disintegration level.

Moreover, the document EP-A-803245 describes aqueous solid compositions containing thermoreversible polysaccharides, a humectant and a powdery phase which
20 may comprise pigments. However, such gels do not have a satisfactory disintegration level.

Accordingly, the need remains for a solid aqueous gel which does not have the disadvantages of the prior art.

25 The Applicant has discovered, unexpectedly, that by combining a particular hydrophilic thickener, namely a cellulose derivative, with a hydrophilic

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gelling agent, and doing so in defined proportions, it is possible to produce solid aqueous gels comprising pigments and/or pearlescent agents, these gels being moreover homogeneous and stable, and being capable of
5 disintegrating easily on the finger or on a sponge or directly on the skin of the face or of the body.

This result is surprising; indeed, the combination of a thickener with a gelling agent usually contributes towards increasing the hardness of a gel
10 which indeed becomes solid, but also crumbly and brittle and often too hard and does not allow good application and low disintegration. The combination claimed below, with a particular hydrophilic thickener such as a cellulose derivative, makes it possible to
15 obtain a solid composition having ideal properties both in terms of stability and disintegration.

The present invention therefore relates to a solid aqueous gel, characterized in that it comprises
i) at least one hydrophilic gelling agent, ii) at least
20 one cellulose derivative and iii) a pulverulent phase comprising at least one pigment and/or one pearlescent agent, the combination of the hydrophilic gelling agent and of the cellulose derivative being present in the gel in an amount of less than or equal to 20% by weight
25 relative to the total weight of the gel.

The gels of the invention exhibit excellent application and disintegration qualities. In

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particular, by virtue of the combination according to the invention, a disintegration level is obtained, for an equivalent hardness, which is greater than that of known sticks. The product is easy to collect, this can
5 be achieved directly on the body or with the finger or with a sponge, by removing a sufficient quantity of product, which is then easy to apply to the skin in a homogeneous manner without requiring preliminary wetting. The make-up obtained is uniform and
10 homogeneous.

These gels are stable over time and with regard to temperature. Thus, after having been stored for two months at room temperature or at 45°C, they exhibit no phenomenon of syneresis (exudation) or phase
15 separation; their appearance and their hardness did not vary.

The gels according to the invention do not become exuded, even for low levels of gelling agent, and they do not necessarily require the use of a
20 special preparation technique. They offer upon application a feeling of great freshness while preserving good cosmetic properties, in particular properties of smoothness.

The subject of the present invention is also
25 a make-up product for the skin or the keratinous fibres comprising a gel as defined above.

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The subject of the present invention is also a method for applying make-up to the skin and/or the keratinous fibres, consisting in applying to the skin and/or the keratinous fibres a make-up gel and/or
5 product as defined above.

For the purposes of the present invention, the expression solid gel is understood to mean a gel having a hardness which is defined by a maximum load before breaking ranging from 5 to 50 grams, at room
10 temperature (20-25°C), after penetration by a stainless-steel rotor 2 mm in diameter in the matrix of the composition at a thickness of 1 mm at a speed of 1 mm/s and withdrawal of the said rotor from the matrix of the composition at a speed of 2 mm/s, the maximum
15 load before breaking being measured with a texture analyser of the "TAXT2" type marketed by the company RHEO.

Preferably still, the maximum load before breaking ranges from 7 to 40 g.

20 The gel according to the invention comprises a hydrophilic gelling agent. The expression gelling agent is understood to mean a compound which, in the presence of a solvent, creates intermacromolecular bonds which are strong to a greater or lesser degree,
25 thus inducing a three-dimensional network which immobilizes the said solvent.

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This hydrophilic gelling agent may be chosen from polysaccharides, protein derivatives, synthetic or semisynthetic gels of the polyester, in particular sulphonic, type, polyacrylates or polymethacrylates and derivatives thereof.

Among the polysaccharides, there may be mentioned:

- extracts of algae such as agar, carrageenans (iota, kappa, lambda), alginates, in particular of Na or Ca;
- exudates of microorganisms such as xanthan gum and its derivatives such as the product sold under the trade name "Rhéosan" by the company Rhodia Chimie, gellan;
- fruit extracts such as pectins;
- gelling agents of animal origin such as bovine or fish protein, in particular gelatin, derivatives, caseinates;
- polysaccharides possessing a side chain and 6 neutral sugars as described in the document FR-A-2759377;
- and mixtures thereof.

Among the synthetic or semisynthetic gels, there may be mentioned the copolyesters described in application FR-A-2 760 643.

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Preferably, the hydrophilic gelling agent is chosen from polysaccharides, preferably still from gellan, carrageenans and mixtures thereof.

As products which are particularly suitable for the invention, there may be mentioned the gellan gum sold under the trade name "Kelcogel F" by the company NUTRASWEET-KELCO or alternatively the ioda-carrageenan sold under the trade names "Seaspen PF 357" or "Viscarin SD 389" by the company FMC.

10 The hydrophilic gelling agent is present in the gel according to the invention at a concentration which makes it possible to obtain, in combination with the cellulose derivative, the hardness and the consistency which are suitable for an ideal
15 disintegration. The hydrophilic gelling agent is preferably present in the gel according to the invention at a concentration which may range from 0.1 to 19.9%, preferably still from 0.2 to 10%, by weight relative to the total weight of the gel.

20 The gel according to the invention also comprises a cellulose derivative. This derivative may for example be chosen from:

- cellulose, carboxymethyl cellulose,
hydroxypropyl cellulose, methyl cellulose,
25 hydroxypropyl methyl cellulose or hydroxyethyl cellulose as well as celluloses which are modified in particular by grafting an alkyl group.

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Preferably the cellulose derivative is carboxymethyl cellulose.

As a cellulose derivative which is particularly suitable for the invention, there may be
5 mentioned:

- sodium carboxymethyl cellulose sold under the trade name "Blanose 7 LF" by the company Aqualon,
- hydroxyethyl cellulose sold under the trade name "Natrosol 250 HHR" by the company Aqualon,
- 10 - hydroxypropyl cellulose sold under the trade name "KLUCEL H" by the company Aqualon,
- cetyl hydroxyethyl cellulose sold under the trade name "Polysurf 67" by the company AQUALON.

The cellulose derivative is present in the
15 gel according to the invention at a concentration which makes it possible to obtain, in combination with the hydrophilic gelling agent, the hardness and the consistency which are appropriate for an ideal disintegration. Preferably, the cellulose derivative is
20 present in the gel according to the invention at a concentration which may range from 0.1 to 10% relative to the total weight of the gel.

The combination of the hydrophilic gelling agent and of the cellulose derivative is present in the
25 gel according to the invention at an overall level which makes it possible to obtain the hardness and the consistency which are appropriate for an ideal

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disintegration, namely a hardness, measured as described above, defined by a load ranging from 5 to 50 g and preferably from 7 to 40 g. Thus, this overall level ranges up to 20% by weight relative to the total weight of the gel.

For example, for a gellan level of 0.5% by weight relative to the total weight of the gel, a carboxymethyl cellulose level of between 0.5 and 1.8%, and even better between 0.5 and 1.3% by weight relative to the total weight of the gel makes it possible to obtain a gel having the hardness and the consistency which are ideal for good disintegration.

The gel according to the invention also comprises a pulverulent phase which comprises at least one pigment and/or one pearlescent agent.

The term pigments should be understood to mean white or coloured, inorganic or organic particles which are insoluble in the medium and which are intended to colour and/or opacify the composition.

The pigments may be present in an amount of 0-40% by weight relative to the total weight of the gel, preferably in an amount of 0.1 to 30% and preferably still in an amount of 1-20%. They may be white or coloured, inorganic and/or organic, of the usual or of a nanometric size. The expression nanometric size is understood to mean pigments whose mean particle size ranges from 5 to 100 nm.

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There may be mentioned, among the inorganic pigments and nanopigments, titanium, zirconium or cerium dioxides, as well as zinc, iron or chromium oxides, nanotitaniums, ferric blue and/or mixtures thereof. Among the organic pigments, there may be mentioned carbon black, and the lacquers commonly used to confer a make-up effect on the lips and on the skin, which are calcium, barium, aluminium or zirconium salts, acid dyes such as halo-acid, azo or anthraquinone dyes and/or mixtures thereof.

The pigments may in particular be coated with silicone compounds such as PDMSs and/or with polymers, in particular polyethylenes, or alternatively with fluorinated compounds. There may thus be mentioned the SA pigments from Maprecos or the PI pigments from Myoshi.

The expression pearlescent agents should be understood to mean iridescent particles which reflect light.

The pearlescent agents may be present in the gel in an amount of 0-40% by weight, preferably in an amount of 0.1 to 30% and preferably still in an amount of 1-20% by weight.

Among the pearlescent agents which may be envisaged, there may be mentioned natural pearl, mica coated with titanium oxide, iron oxide, natural pigment

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or bismuth oxychloride as well as coloured mica-titanium.

In general, the pulverulent phase comprises enough pigments and/or pearlescent agents to provide
5 the desired make-up effect. Thus, preferably, the aqueous gel according to the invention is not transparent, that is to say that it is not possible to see the characters on a newspaper page through the gel. Preferably still it is not translucent, that is to say
10 that it does not allow the passage of light.

The pulverulent phase preferably comprises from 0.1 to 40%, preferably still from 0.1 to 20% by weight, relative to the total weight of the gel, of pigments and/or pearlescent agents.

15 The pulverulent phase of the gels according to the invention may comprise, in addition, fillers.

The term fillers should be understood to mean colourless or white, inorganic or synthetic, lamellar or nonlamellar particles intended to give the
20 composition body or stiffness, and/or the make-up smoothness, mattness and uniformity.

The fillers, which may be present in the gel in an amount of 0-60% by weight relative to the total weight of the gel, preferably in an amount of 0.1 to
25 40%, preferably still 1-20%, may be inorganic or synthetic, lamellar or nonlamellar.

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There may be mentioned talc, mica, silica, kaolin, Nylon powder, poly- β -alanine powder and polyethylene powder, Teflon, lauroyllysine, starch, boron nitride, bismuth oxychloride, tetrafluoroethylene

5 polymer powders, polymethyl methacrylate powders, polyurethane powders, polystyrene powders, polyester powders, synthetic hollow microspheres, microsponges, microbeads of silicone resin, zinc and titanium oxides, zirconium or cerium oxides, precipitated calcium

10 carbonate, magnesium carbonate and hydrocarbonate, hydroxyapatite, hollow silica microspheres, glass or ceramic microcapsules, metallic soaps derived from organic carboxylic acids having from 8 to 22 carbon atoms, preferably from 12 to 18 carbon atoms, such as

15 zinc, magnesium or lithium stearate, zinc laurate, magnesium myristate, the compounds $\text{SiO}_2/\text{TiO}_2/\text{SiO}_2$, $\text{TiO}_2/\text{CeO}_2/\text{SiO}_2$ or $\text{TiO}_2/\text{ZnO}/\text{talc}$, and polymers of polyethylene terephthalate/polymethacrylate in the form of flakes.

20 It is possible to modify the stiffness of the gels according to the invention by adding thereto one or more salts which will increase this stiffness. These salts may be chosen from mono-, di- or trivalent metal salts, and more particularly alkali and alkaline earth

25 metal salts and in particular sodium, calcium or magnesium salts. The ions which constitute these salts may be chosen, for example, from carbonates,

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bicarbonates, sulphates, glycerophosphates, borates, chlorides, nitrates, acetates, hydroxides, persulphates as well as the salts of α -hydroxy acids (citrates, tartrates, lactates, malates) or of fruit acids, or
5 alternatively the salts of amino acids (aspartate, arginate, glycocholate, fumarate). The quantity of salt may range from 0.01 to 2% and preferably from 0.1 to 1% of the total weight of the gel.

Preferably, the salt is chosen from calcium,
10 magnesium or strontium nitrate, calcium or magnesium borate, calcium, sodium, magnesium, strontium, neodymium or manganese chloride, magnesium or calcium sulphate, calcium or magnesium acetate, and mixtures thereof. Preferably still, the salt is magnesium
15 chloride.

The gels of the invention contain, in addition, a cosmetically or physiologically acceptable medium, that is to say a medium which is compatible with all keratinous materials such as the skin, nails,
20 hair, eyelashes and eyebrows, mucous membranes and semimucous membranes, and any other skin area of the body and of the face.

The gels according to the invention may also comprise floral water such as cornflower water and/or
25 mineral water such as VITTEL water, LUCAS water or LA ROCHE POSAY water and/or thermal water.

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The gels according to the invention may also comprise water-soluble colorants chosen from the customary colorants in the field considered, such as the disodium salt of ponceau, the disodium salt of alizarin green, quinoline yellow, the trisodium salt of amaranth, the disodium salt of tartrazine, the monosodium salt of rhodamine, the disodium salt of fuchsin, or xanthophyll.

Preferably, the gels according to the invention comprise up to 99.8% by weight, preferably from 20 to 99% by weight, relative to the total weight of the gel, of water.

The gels according to the invention may also comprise solvents other than water, such as for example primary alcohols such as ethanol and isopropanol, glycols such as propylene glycol, butylene glycol, dipropylene glycol, diethylene glycol, glycol ethers such as (C₁-C₄)alkyl ethers of mono-, di- or tripropylene glycol, mono-, di- or triethylene glycol, and mixtures thereof.

The gels of the invention may comprise, in addition, any additional hydrophilic compound customarily used in the cosmetics field. These additional compounds may be chosen from antioxidants, preservatives, hydrophilic cosmetic or pharmaceutical active agents, moisturizers, vitamins, self-tanning

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compounds such as DHA, sunscreens, perfumes, and mixtures thereof.

These additional compounds may be present in the gel in an amount of 0-10% by weight.

5 Of course, persons skilled in the art will be careful to choose this or these possible additional compounds, and/or their quantity, in a manner such that the advantageous properties of the gel according to the invention are not, or not substantially, adversely
10 affected by the envisaged addition.

Preferably, the gels according to the invention are free of liquid fatty substances such as oils. Preferably still, they are free of a fatty phase.

15 The gels according to the invention may be prepared according to conventional methods for preparing sticks, these methods being well known to persons skilled in the art.

20 The gels according to the invention may constitute make-up or health care products for the skin, in particular the body, the face and/or the scalp, or the keratinous fibres, in particular the hair, the nails, the eyelashes and/or the eyebrows, or the mucous membranes, in particular the lips. They can thus constitute make-up products for the body,
25 foundations, eyeshadows, blushers, concealers, lipsticks, pencils for the contour of the lips,

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mascaras, pencils for the contour of the eyes, dyeing or make-up sticks for locks of hair.

The invention is illustrated in greater detail in the following examples.

5 In the following examples, the quantities are given as a percentage by weight relative to the total weight of the composition.

EXAMPLE 1:

10 The Applicant produced the aqueous gel in the form of the following foundation stick:

- Gellan gum sold under the trade name	0.5%
"Kelcogel F" from NUTRASWEET-KELCO	
- Mg chloride	0.1%
- Sodium carboxymethyl cellulose sold under the	1.2%
trade name "Blanose 7 LF" by the company	
Aqualon	
- Preservative	qs
- Pigments (iron oxides and titanium dioxide)	7%
- Propylene glycol	7%
- Water	qs 100%

15 This gel was prepared in the following manner: the water and the preservative were heated to 90°C, and then the gellan was incorporated with stirring. After waiting for 15 min, the carboxymethyl cellulose was incorporated with stirring, and then the pigmentary paste produced beforehand by mixing the pigments with propylene glycol.

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The mixture was subsequently poured into a dish and then cooled. The whole is allowed to stand for 24 h at room temperature.

A stick is obtained which is very fresh upon application, which can be used with a dry or wet sponge, which can be collected well and which can be easily and homogeneously applied to the skin.

The application of make-up to the skin with such a stick gives a natural and transparent result, totally free of greasy effect.

The hardness of this gel, measured as described above, is 14 g.

EXAMPLE 2:

The Applicant produced the following aqueous gel in the form of a stick for tattooing the body:

- Lambda-carrageenan sold under the trade name "Satia gum UTC 10" by FKW Biosystems 5%
- Gellan gum sold under the trade name "Kelcogel F" from NUTRASWEET-KELCO 0.5%
- Sodium carboxymethyl cellulose sold under the trade name "Blanose 7 LF" by the company Aqualon 1.2%
- Preservative qs
- Water qs 100%
- Pearlescent agents 5%

This stick was prepared in the same manner as in Example 1.

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A stick is obtained which can be used directly on the skin, which disintegrates well so as to draw motifs or lines on the body.

The hardness of this stick, measured as
5 described above, is 5.6 g.

The Applicant also produced the gel of Example 2 without carboxymethyl cellulose: such a gel has a hardness of 7.4 g, but it disintegrates with difficulty.